

Bond Formation at the Alkali-Metal/Metal Interface

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Alkali metal growth on transition metals has very important applications in catalysis. Yet the interaction between isolated alkali metal atoms and metallic substrates is not completely understood, even without the complications of interactions between alkali atoms or alkali/gas molecules on these surfaces. For example, since the introduction of the Langmuir-Gurney model (LG) in 1935, the explanation of the large work function shift for metal substrates when covered by submonolayers of Alkali Metals (AM) was thought to be well understood in terms of a simple charge-transfer picture: at low coverages the AM donates its lone *s*-electron to the substrate, creating a large surface dipole layer, which lowers the work function. As coverage increases towards one monolayer (ML), the AM atoms interact, and the resulting dipole-dipole repulsion drives a charge transfer back from the substrate to the alkali *s*-level, a process called back-donation. This back-donation is thought to account for the characteristic minimum in the work function followed by recovery with higher coverage.

While providing a satisfactory explanation of experiment for over 50 years, this model has recently come under question from both experimental and theoretical work. While there is consensus that the work function change is due to a net surface dipole, the issue becomes: where is the dipole located? If the dipole is due to a complete charge transfer from the AM to the substrate, the AM is left with an unoccupied *s* valence level at low coverage, which becomes occupied at higher coverages. If, on the other hand, the dipole is localized within the AM atom, there should be an occupied *s*-derived valence state observable at all coverages. A clear signature for *s*-derived valence band features has been lacking (at least for growth on transition metals), however, due to the presence of substrate *d*-bands.

To clarify these issues, we undertook a detailed study of the growth of Li on Mo(110) surface.

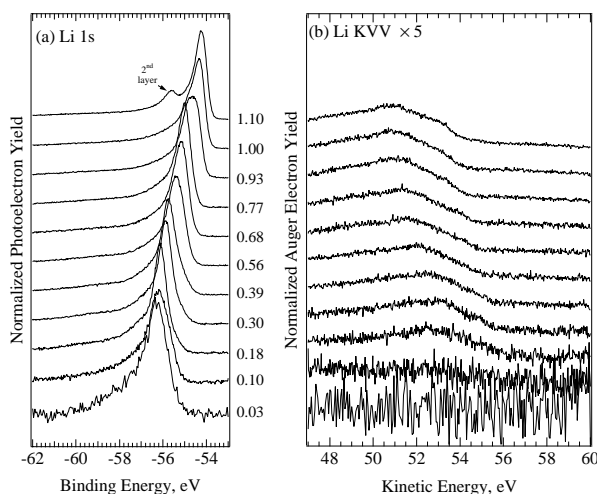


Fig. 1. (a) Core level and (b) Auger decay spectra as a function of Li coverage on Mo(110). The numbers in (a) indicate the approximate Li coverage in ML. The data are shown normalized to Li 1s intensity, in order that the Auger intensity is normalized per Li atom.

The data were acquired using undulator-generated soft x-rays at beamline 7.0 of the ALS. By measuring the valence bands, work function, and Auger decay cross section as a function of coverage up to a monolayer of Li on Mo(110), we directly deduce the relative population of AM valence *s*-orbital vs. coverage. To first order, the LG model seems to be vindicated, although important questions remain.

Fig. 1(a) shows a series of Li 1s core-level spectra as a function of Li coverage. The data have been normalized to Li 1s area, which is proportional to the number of Li atoms deposited. In (b) we show an additional peak, whose kinetic energy is independent of photon energy, which we identify as Li KVV (core - valence - valence) Auger

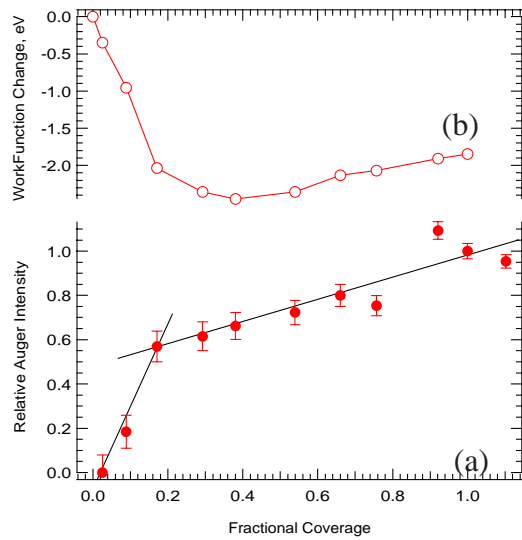


Fig. 2. (a) Normalized Auger yield per Li atom and (b) workfunction change as a function of Li coverage on Mo (110).

angle-resolved valence band photoemission for the clean surface. The bands marked “*d*” are substrate *d*-like surface states. Fig. 3(b) shows that at 1 ML coverage, the *d*-states have moved significantly down in energy, due to the change in potential at the interface. In addition, a weak, broad band labeled “*s*” is observed. We identify this band with the Li 2*s* states, whose excitation in the presence of the Li 1*s* core hole accounts for the Auger decay intensity discussed above. For intermediate coverages, between clean and 1 ML, the *s*-level is observed to pass down from above the Fermi level. In fact, the first appearance of this band exactly coincides with the appearance of the Auger decay.

Significant questions remain, however, suggesting our interpretation is incomplete. First, the formation of the auger decay peak is essentially complete well before the minimum in the workfunction. Second, the width of the auger peak is significantly wider than the *s*-band we observe in fig. 3(b), suggesting a more atomic-like multiplet final state inconsistent with the band

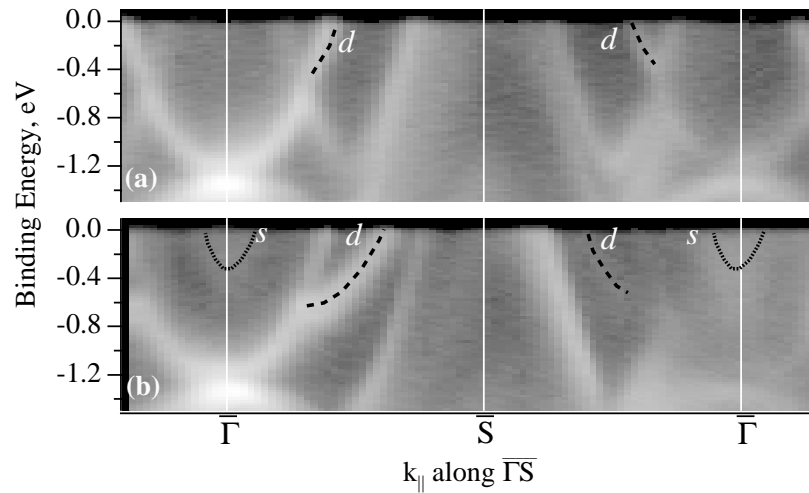


Fig. 3. Bandmaps for (a) clean and (b) 1 ML Li on Mo (110). The surface states *s* and *d* are assigned to Li 2*s*-like and Mo 4*d*-like states, respectively.

decay, and which we also show normalized to Li coverage. Clearly, the relative yield of this emission varies dramatically with coverage. Fig 2(a) shows how the Auger yield per Li atom varies with coverage. For comparison, the change in workfunction with coverage is shown in fig. 2(b). Since the Auger yield depends on occupation of the Li 2*s* level, our data gives a direct measure of the charge state of the Li atom. Hence, it would seem that the LG model is quite compatible with our data: while at low coverage, the 2*s* level is unoccupied (charge has transferred to the substrate), as the coverage increases, Li 2*s* valence states become occupied as charge is donated from the substrate back to the Li atom

We have also measured the valence bands as a function of growth, which gives independent confirmation of this picture. In fig. 3(a), we show

interpretation. Third, an alternate explanation of the Auger behavior is a transition from localized to delocalized Li 2*s* bands, which may be entirely unrelated to charge transfer to the substrate. We are currently working to further understand these issues.

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